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The coordination chemistry of decamethylmetallocene cations of trivalent transition metals

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1 Introduction

1.1 The discovery of metallocene complexes

The first report on a metallocene complex (metallocene: metallon = metal (Greek) + cene = cyclopentadiene (20th century)) originates from 1951 by Kealy and Pauson. The original objective of their research was the synthesis of fulvalene by a reductive coupling of cyclopentadienylmagnesium bromide using iron(III)chloride. Instead, orange crystals were obtained of a compound which had the general formula $C_{10}H_{10}Fe$.¹ Concurrent to Pauson's findings, Miller *et al.* reported the synthesis of the same compound by the reaction of cyclopentadiene with iron in the presence of aluminum, potassium or molybdenum oxides.² The structure of this, at that time highly unusual, compound was resolved not much later by Fisher, Woodward and Wilkinson, and consists of an iron(II) center trapped between two parallel cyclopentadienyl ligands in which the carbon atoms of the cyclopentadienyl rings are equally bound to the metal center (Figure 1.1).^{3,4}

The discovery of ferrocene (ferrocene: ferrum = iron (Latin)), which had been prepared unwittingly on previous occasions during the iron catalyzed cracking of dicyclopentadienyl,⁵ has led to a true run on other metallocene complexes of transition

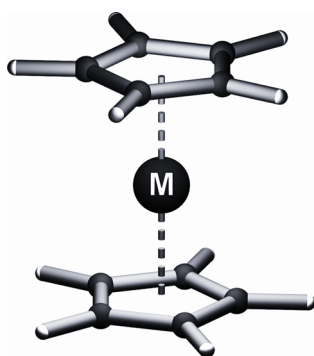


Figure 1.1. Ball-stick representation of the structure of a metallocene.

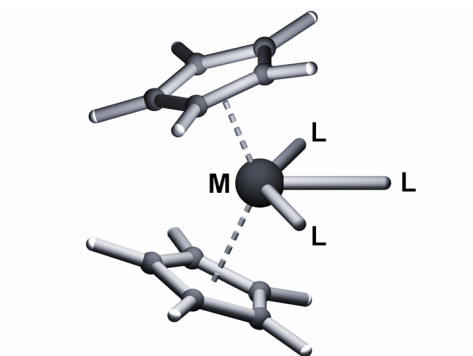


Figure 1.2. Ball-stick representation of the bent metallocene geometry (M = metal center; L = ligand).

metals.⁶ In case of complexes of the type $\text{Cp}_2\text{M(II)}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), the geometry is generally as depicted in Figure 1.1,⁷ but when additional ligands are bound to the metal center, the cyclopentadienyl ligands will yield, resulting in a bent structure (Figure 1.2).

In metallocene complexes, the cyclopentadienyl ligand is mostly η^5 -coordinated to the metal center, donating 6 electrons, but there are numerous examples, especially in case of main group metals, of η^1 , η^2 or η^3 coordination and also of σ -bound cyclopentadienyl ligands (Figure 1.3).⁸

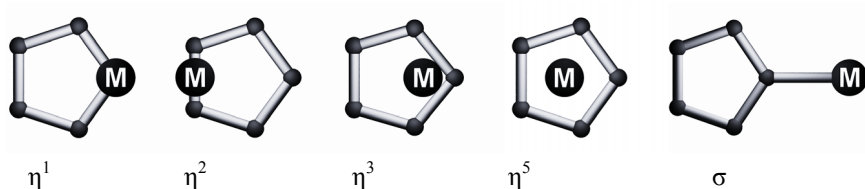
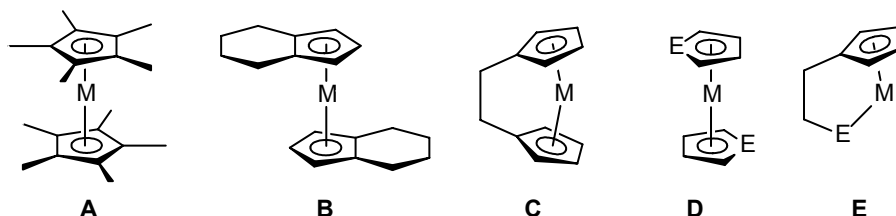


Figure 1.3. Bonding modes for the cyclopentadienyl ligand.

1.2 Early transition metal metallocene complexes in catalysis

Concurrent with the first report on metallocene complexes, Ziegler and coworkers reported that TiCl_3 in combination with aluminum alkyl complexes is very active in the polymerization of ethene.⁹ Natta showed that this heterogeneous catalyst system is also active in the isotactic polymerization of propene.¹⁰ Before long Breslow and coworkers

Scheme 1.1



demonstrated that titanocene dichloride could also be used as catalyst for the polymerization of olefins when activated in a similar way as in the heterogeneous system described by Ziegler and Natta,¹¹ although the polymerization activity was very low. Much later, in 1980, Kaminsky and Sinn reported the use of methylaluminoxane as an activator (see also chapter 1.3).¹² This resulted in much more active olefin polymerization catalyst, and led to comprehensive developments in the field of metallocene chemistry, especially of group 4 metals.¹³ As a result the cyclopentadienyl ligand has been subject to a wide variety of modifications (Scheme 1.1), such as the introduction of substituents to the cyclopentadienyl ring (**A**), annulated ring systems (**B**), the linking of two cyclopentadienyl ligands (**C**), the substitution of one or more carbon atoms by heteroatoms (**D**), or the replacement of one of the cyclopentadienyl ligands by other ligands (**E**).^{13,14,15,16}

Whereas the search for more active and selective olefin polymerization catalysts has been a dominant drive in the developments in metallocene chemistry, and in organometallic chemistry of early transition metals in general, many other applications have evolved from this type of complexes. Metallocenes have been used in the addition of X-H bonds (X = B, N, Si, P, Sn) to unsaturated hydrocarbons,¹⁷ in cycloaddition reactions, like olefin metathesis and hydroamination reactions,^{17a,d} but also in the reductive coupling of unsaturated compounds^{17a,18} or the activation of C-X bonds.¹⁹

1.3 Cationic early transition metal metallocenes

In general, the active species in the catalytic polymerization of olefins is an electron deficient transition metal complex with a reactive metal-carbon bond.¹³ Whereas neutral olefin polymerization catalysts have been reported,²⁰ most examples involve cationic complexes. As mentioned above, a convenient and frequently used method to obtain

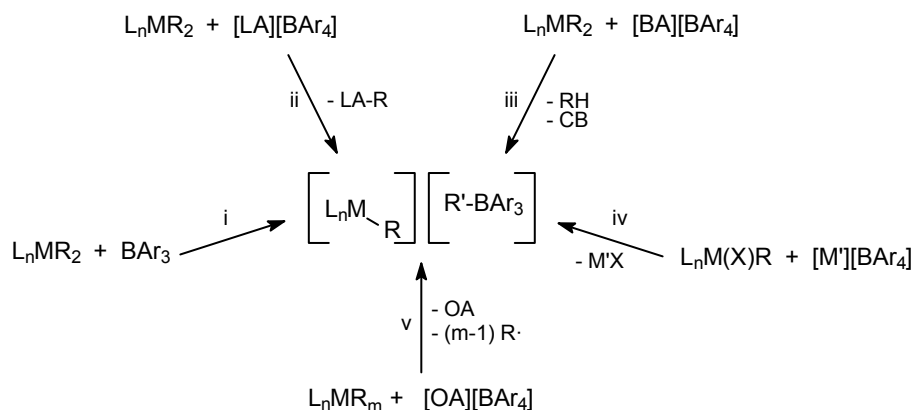
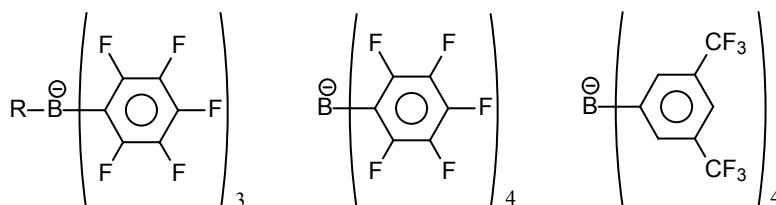


Figure 1.4. Routes to well-defined, cationic, early transition metal complexes. L = ancillary ligand; M = early transition metal; R = alkyl ligand; Ar = aryl group; LA = Lewis acid; BA = Brønsted acid; CB = conjugated base; M' = Li, Na, Ag; X = halogen; OA = oxidant.

this type of transition metal complexes is the reaction of a metallocene dihalide with methylaluminoxane (MAO), in which the function of the aluminoxane is twofold: it acts both as an alkylating agent and as a Lewis acid that abstracts one of the alkyl ligands from the metal to yield a cationic complex with a weakly coordinating anion.^{12,21} A major drawback of MAO as activator is the need of a large excess of the cocatalyst (Al/M ratio > 200). An additional disadvantage from a fundamental research point of view is the fact that MAO is ill defined. It is known that MAO consists of a (dynamic) mixture of cage-like oligomers with the general formula $[MeAlO]_n$. Even though many research groups are trying to identify its exact nature and function, details remain under much debate.^{21,22}

As a consequence, alternative routes to well-defined transition metal cations have been developed (Figure 1.4).^{21,23} The majority is based on arylborane (i, Figure 1.4)²⁴ and -borate (ii-v, Figure 1.4)^{25,26,27,28} reagents affording ion pairs with a tetrasubstituted borate anion. The nature of the counterion has a surprisingly large effect on both the activity and the selectivity of olefin polymerization catalysts.^{13,21,29} The most active catalysts were obtained when weakly coordinating anions were applied. This inspired many research groups to develop this type of anions,^{21,30} many of which employ

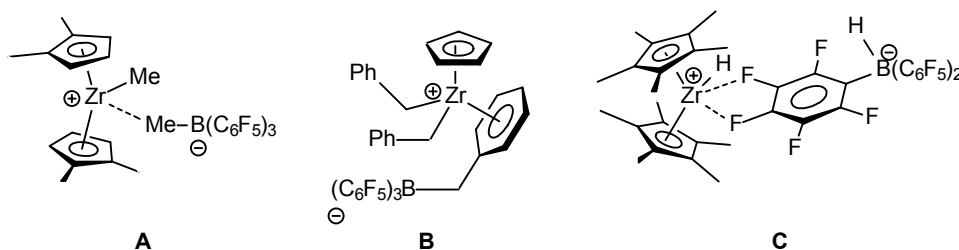
Scheme 1.2



fluorinated groups to dissipate the negative charge, to reduce Coulombic interactions, and to decrease their nucleophilicity. Three anions of this type, which are most frequently applied, are depicted in Scheme 1.2.^{24,31}

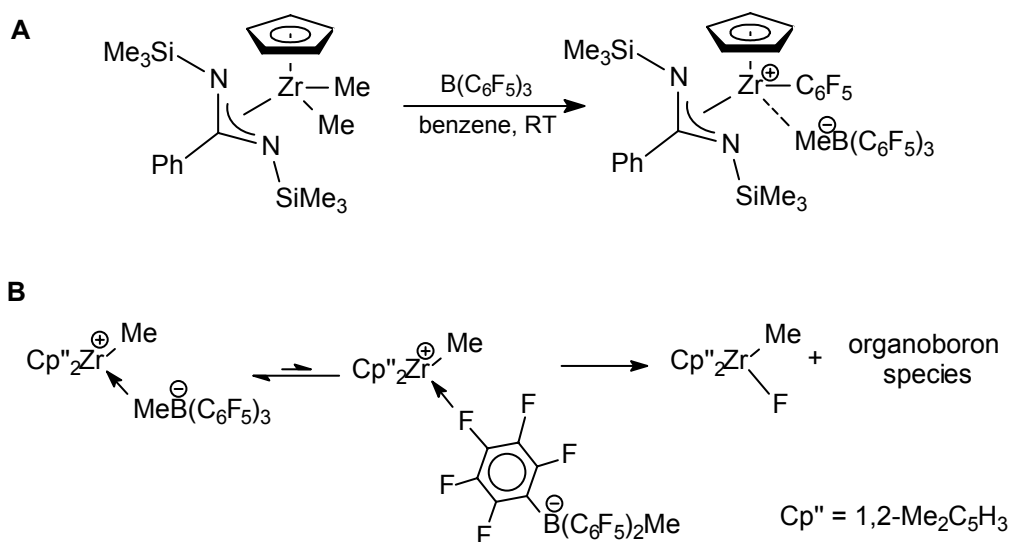
Fluorinated arylborate anions can still exhibit interactions with the metal center and participate in catalyst deactivation reactions. In case of an alkyltrispentafluorophenylborate anion, generated in the reaction of a metal alkyl complex with a Lewis acidic borane reagent (i, Figure 1.4), the counterion can coordinate to the metal center via the abstracted alkyl group (**A**,³² **B**,³³ Scheme 1.3). Well documented examples in which such a fluorinated arylborate anion is bound with one or more fluorine atoms to the metal center are limited (**C**, Scheme 1.3).^{32,34}

Scheme 1.3



Apart from influencing the reactivity of early transition metal complexes, the anion can also be involved in catalyst deactivation reactions. Degradation of the ion-pair commonly involves the transfer of one of the groups from the borate anion to the metal center (**A**, Scheme 1.4),³⁵ but there is one example in which C-F bond activation of the fluorinated borate anion is observed (**B**, Scheme 1.4).³²

Scheme 1.4



1.4 Objective

The highly electron deficient metal complexes mentioned above are very susceptible to the coordination of Lewis-bases. In addition they react, as a result of their high electrophilicity, with functions that are generally regarded as weakly or non-coordinating, such as C-H³⁶ and C-X bonds (X = F, Cl, Br).³⁷ Regardless of the weak nature of the binding of these substrates, they can have a large effect on the reactivity of these complexes. The research presented in this thesis is aimed at the understanding of this type of weak interactions, and especially at the effect of the electron configuration of the metal on these interactions. Our investigations are focused on the reactivity of the trivalent, cationic decamethylmetallocene complexes $[\text{Cp}^*_2\text{M}]^+$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; M = Sc, Ti, V). These have a close resemblance to well-known olefin polymerization catalysts, with the difference that they lack the very reactive metal-carbon bond.

The metallocenes described in this thesis range from d^0 to d^2 metal complexes. The three frontier orbitals that determine the reactivity of these bent metallocene complexes

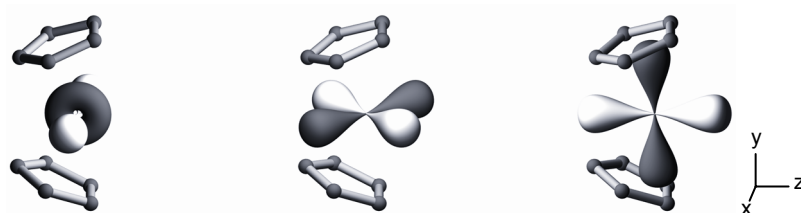


Figure 1.5. Simplified representation of the three frontier orbitals of a bent metallocene framework

Table 1.1. Characteristics of the $[\text{Cp}^*_2\text{M}]^+$ cation ($\text{M} = \text{Sc}, \text{Ti}, \text{V}$)

| | Sc | Ti | V |
|-------------------------------------|--------|-------------------|---------|
| Valence electrons | 12 | 13 | 14 |
| spin state | $S=0$ | $S = \frac{1}{2}$ | $S = 1$ |
| free valence orbitals | 3 | 2 | 1 |
| ionic radius of $\text{M}(3+)^{39}$ | 0.75 Å | 0.67 Å | 0.65 Å |

are a d_{x^2} , a d_{xz} and a $d_{y^2-z^2}$ like orbital (Figure 1.5).³⁸ In case of a d^0 metallocene cation, such as $[\text{Cp}^*_2\text{Sc}]^+$, these three frontier orbitals are, in principle, all available for the interaction with additional ligands and in case of the d^1 titanocene cation, one of these orbitals is occupied by an unpaired electron, leaving two free valence orbitals. In case of the vanadocene cation, a d^2 system with $S=1$, one free valence orbital is left for the binding of additional ligands (Table 1.1).

In principle the coordination chemistry of these metallocene complexes can be influenced by the presence of unpaired electrons in two ways. In case of the d^1 titanocene and d^2 vanadocene cations the unpaired electrons may have a weakening

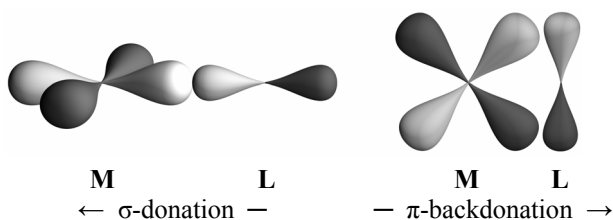


Figure 1.6. Chatt-Dewar-Duncanson-model: ligand to metal σ -donation (left) and metal to ligand π -backdonation (right).

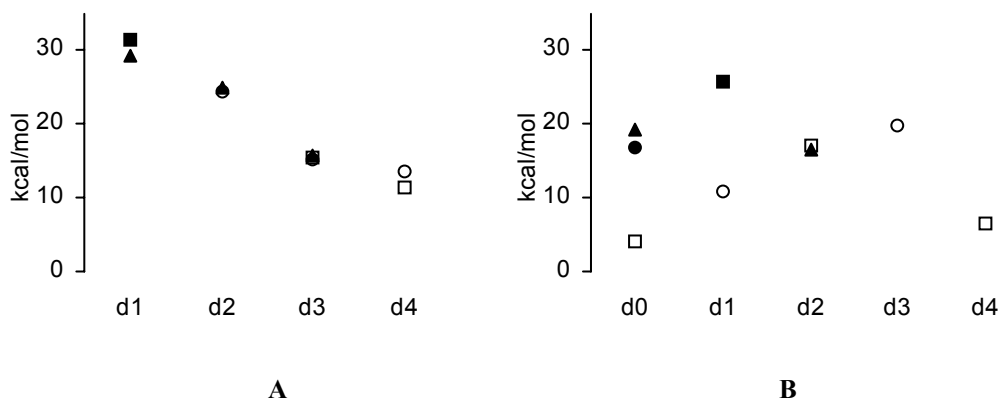


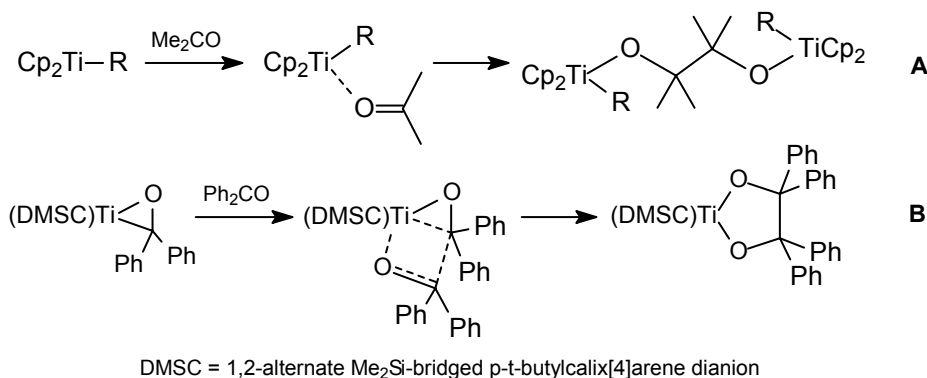
Figure 1.7. The relative binding enthalpies of ethene determined with DFT calculations for (A) $[LL'MR]^+$ ($L = \text{NH}_2, \text{NH}_3$; $L' = \text{NH}_2, \text{NH}_3$) and (B) $[\{\text{Cp}(\text{CH}_2)_2\text{NH}_2\}\text{MMe}]^+$ (\bullet Sc, \blacksquare Ti, \blacktriangle V, \circ Cr, \square Mn).

effect on the binding energy of additional ligands. On the other hand, the singly occupied orbitals may contribute to the binding through π -backdonation (Figure 1.6).⁴⁰ The overall effect of the unpaired electrons on the binding energy will be a fine balance between these two effects and is dependent on the relative energies of the SOMO(s) and the LUMO, thus on the coordination sphere of the transition metal complex.

This is illustrated by two independent theoretical studies to the effect on unpaired electrons on the binding of ethene.⁴¹ In the first, the $[LL'MMe]^+$ ($L = \text{NH}_2, \text{NH}_3$; $L' = \text{NH}_2, \text{NH}_3$; $M = \text{Ti} - \text{Mn}$) system was considered.^{41a} The energy associated with the binding of ethene showed a linear decrease with the number of unpaired valence electrons (A, Figure 1.7). Furthermore, the binding energy in olefin complexes with the same electronic configuration was comparable, e.g. the energy associated with the binding of ethene to the d^3 metal cations $[(\text{NH}_3)_2\text{VMe}]^+$, $[(\text{NH}_2)(\text{NH}_3)\text{CrMe}]^+$, and $[(\text{NH}_2)_2\text{MnMe}]^+$ is very similar (15.7, 15.1 and 15.6 kcal/mol respectively). Such a trend was not found in the second study, in which the effect of unpaired electrons on the coordination of ethene was considered in the $[\{\text{Cp}(\text{CH}_2)_2\text{NH}_2\}\text{MMe}]^+$ system (B, $M = \text{Sc} - \text{Mn}$; Figure 1.7).^{41b}

Beside the effect that unpaired electrons can have on the coordination of substrates, they can also enable reactions that would otherwise be inaccessible. For example,

Scheme 1.5



d^1 -titanocene complexes are known to couple unsaturated compounds, such as ketones (A, Scheme 1.5),⁴² whereas this type of pinacol coupling has not been observed in the analogous d^0 -metal complexes. Furthermore, d^2 -metal complexes can effectuate a similar coupling via the insertion of a ketone into an η^2 -bound ketone adduct (B, Scheme 1.5).

1.5 Overview

The chemistry described in this thesis has a focus on the reactivity of the metallocene cations towards C-F bonds, but in chapter 2 the synthesis of the cationic decamethylmetallocene THF adducts will be discussed. These THF adducts give fundamental insight in the general coordination chemistry of this type of metallocene cations with Lewis bases, and can be used as a reference to the base-free metallocene cations and the weak adducts described in chapter 4. These are generally insoluble and reactive towards most solvents, impeding more direct methods of characterization.

In chapter 3 the synthesis and structure of the base-free metallocene cations are described. The structure of the $[\text{Cp}^*_2\text{M}][\text{BPh}_4]$ salts show interactions with either the counterion ($\text{M} = \text{Sc}$) or with Cp^* -methyl groups ($\text{M} = \text{Ti}, \text{V}$). Such an agostic interaction has not been observed before with methyl groups of substituted Cp-ligands.

Chapter 4 addresses the reactivity of the cationic metallocene complexes towards C-F bonds. First the reaction with neutral organofluorides is described. The metallocene complexes of scandium and titanium react with fluorobenzene to form stable fluorobenzene adducts, and in a similar way, these metallocene cations react with 1,2-difluorobenzene to yield adducts in which both fluorine atoms are coordinated to the metal center. These fluorobenzene adducts were characterized by single crystal X-ray diffraction studies and are to our knowledge the first structurally characterized complexes of this type. DFT calculations indicate that the interaction of the $[\text{Cp}^*_2\text{M}]$ cations with the fluorobenzenes is weak, and mainly electrostatic in nature. Whereas the metallocene cations are stable towards $\text{C}(\text{sp}^2)\text{-F}$ bonds, the scandocene and titanocene cations readily react with benzylic C-F bonds to yield Cp^*_2ScF and $\text{Cp}^*_2\text{TiF}_2$, respectively.

To extend these results, the stability of the metallocene cations with the $[\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{B}\{\text{C}_6\text{H}_3(3,5\text{-CF}_3)_2\}_4]$ anions was studied. The first has $\text{C}(\text{sp}^2)\text{-F}$ bonds, similar to fluorobenzene and 1,2-difluorobenzene, whereas the latter has benzylic fluorides, similar to α,α,α -trifluorotoluene. Consequently, the ion pair $[\text{Cp}^*_2\text{Ti}][\text{B}(\text{C}_6\text{F}_5)_4]$ is stable, and C-F bond activation is observed in $[\text{Cp}^*_2\text{Ti}][\text{B}\{\text{C}_6\text{H}_3(3,5\text{-CF}_3)_2\}_4]$. In the $[\text{Cp}^*_2\text{M}][\text{B}(\text{C}_6\text{F}_5)_4]$ ion pair of scandium and titanium, the anion is bound to the metal center with two C-F bonds, similar to the molecule of 1,2-difluorobenzene in the 1,2-difluorobenzene adduct. In case of vanadium, no such interaction between the cation and anion was observed.

The reactivity of the $[\text{Cp}^*_2\text{M}]$ cations towards acetone and benzophenone is discussed in chapter 5. The reactivity of the metallocene cations towards acetone results in complexes comparable to the THF adducts ($\text{M} = \text{Sc}$: bis-acetone adduct; $\text{M} = \text{Ti}, \text{V}$: mono-acetone adduct). Their M-O-C bond angles (bent vs. linear) are determined by the electron configuration of the metal center. In case of scandium and titanium the acetone ligand can donate more than two electrons to the metal center, resulting in a linear coordination of acetone. In case of vanadium there is one free valence orbital, which is reflected by a bent M-O-C bond angle. The reaction of the decamethylmetallocene cations with benzophenone resulted in mono-benzophenone adducts, exclusively. In case of the benzophenone adduct of vanadium the unpaired electrons appear to be delocalized into the benzophenone ligand.

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